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A Molecularly-Based Theory for Electron Transfer Reorganization Energy in Solvent Mixtures

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Using statistical field techniques, we develop a molecularly-based dipolar self-consistent-field theory (DSCFT) for charge solvation in liquid mixtures under equilibrium and nonequilibrium conditions, and apply it to compute the solvent reorganization energy of electron transfer reactions. In addition to the nonequilibrium orientational polarization, the reorganization energy in liquid mixtures is also determined by the out-of-equilibrium solvent composition around the reacting species due to preferential solvation. Using molecular parameters that are readily available, the DSCFT naturally accounts for the dielectric saturation effect and the spatially varying solvent composition in the vicinity of the reacting species. We identify three general categories of binary solvent mixtures, classified by the relative optical and static dielectric permittivities of the solvent components. Each category of mixture is shown to produce a characteristic local solvent composition profile in the vicinity of the reacting species, which gives rise to the distinctive composition dependence of the reorganization energy that cannot be predicted using the dielectric permittivities of the homogeneous solvent mixtures.

I. INTRODUCTION

It has long been established that solvent fluctuation plays a central role in the kinetics and dynamics of electron transfer (ET) processes. The groundbreaking work by Marcus in 1956 envisioned fluctuation of solvent orientational polarization on two crossing parabolic nonequilibrium free energy surfaces – whose curvature is determined by a linear dielectric treatment of the solvent – and elucidated the relationship between the free energy for solvent reorganization and the rate of ET processes.[1,2] Since then, the area of ET has seen much research activity and growth,[3,4] for example, with subsequent theoretical work on dynamical[5–12] and quantum-mechanical effects,[13–23] experimental confirmation of the inverted region,[24] and characterization of ET mechanism in proteins and photosynthetic systems.[25–28] However, relatively little attention has been given to solvent mixtures, despite their common usage as solvent media, for instance, in recent developments of lithium-ion batteries.[29] Solvent mixtures are paramount to technological and industrial applications, since they offer virtually endless possibilities as reaction media, allowing continuous tuning of the macroscopic solvent properties for optimal performance. To facilitate the search of new reaction media for technological applications, a convenient and predictive theoretical framework for solvent reorganization in liquid mixtures is desirable.

The lack of understanding for ET processes in solvent mixtures is due in large part to the complex effects mixed solvents have on the ET rates.[30] Experimental studies have shown distinctive behaviors in the ET rates depending on the specific electron transferring species and the solvent components. However, no systematic trend has emerged for understanding the observed behaviors and for predicting the behaviors in general mixtures.[11,31–40] Moreover, the kinetic,[35,41] dynamic,[42,43] and spectroscopic behaviors[44] for ET processes in solvent mixtures cannot be directly correlated with the corresponding properties in the pure solvent components. It is generally recognized that ET in mixed solvents is not controlled by macroscopic solvent parameters because of preferential solvation,[41,44–50] as the local composition of the solvent around a charged solute is significantly different from the bulk composition.[51]

Despite its importance, there have been very few theoretical studies for ET in liquid mixtures. Zusman developed an analytical theory to study the dynamical solvent effect in ET, connecting the ET rate to the solvent diffusion coefficients and the mixture correlation functions.[52] For the solvent reorganization energy, Chandra considered a nonpolarizable solvent mixture model using density functional theory with a constrained variational approach, and found that preferential solvation of the reacting system by the more polar species of the mixture is crucial.[53] One current theoretical challenge, in order to better understand the effect of solvent on ET kinetics, is to take into account the electronic polarizability of the solvent mixture, which is responsible for the solvent induced dipoles that respond on the same time scale as the charge transfer. Furthermore, as mixture correlation functions, which are required inputs in density functional approaches, are not readily available, it is desirable to develop a simple analytical theory based on readily-available pure-solvent properties, which can be efficiently used for surveying the vast number of possible solvent mixtures.

Recently, we developed a molecularly-based dipolar self-consistent-field theory (DSCFT) for calculating reorganization energies in pure liquids using statistical-field techniques.[54] The theory models the polarizable solvent molecules using a few readily-available molecular parameters, including the permanent dipole moment, the polarizability, and the molecular volume. The statistical-

field transformations yield orientational and electronic polarizations of the solvent that are continuous, spatially dependent functions. The resulting theory naturally accounts for the effect of dielectric saturation around the reacting species, and as a result, it is unnecessary to distinguish between the inner-sphere and the outer-sphere solvent molecules in the calculations. Despite the simplicity of the theory, the solvent reorganization energies predicted by the DSCFT, with no adjustable parameters, are in good agreement with previous calculations and experimental measurements for a range of reactions.

In this article, we extend the DSCFT to charge solvation in liquid mixtures under equilibrium and nonequilibrium conditions, and apply the theory to the solvent reorganization energy of ET processes. For ET in solvent mixtures, the slow-responding nuclear degrees of freedom not only relate to the solvent orientational polarization – as in earlier works for pure solvents – but also to the solvent composition around the reacting species. In constructing the nonequilibrium free energy, we keep both the orientational polarization and the solvent composition at their values in the reactant state, and perform a constrained extremization on the free energy with the reacting species at the product state. The resulting theory naturally accounts for the spatially-varying solvent composition and response. Our theory suggests three general categories of binary mixtures, classified by the relative static and optical dielectric permittivities of the solvent components. We explore the relationship between the reorganization energy and the bulk solvent composition in these three mixture categories. We find that each category of mixture produces a distinctive local solvent composition profile in the vicinity of the reacting species, which gives rise to the distinctive composition dependence of the reorganization energy that cannot be predicted using the dielectric permittivities of the homogeneous solvent mixtures.

The rest of the article is organized as follows. In Section II, we present the formulation of the DSCFT for solvation of a general solute under both equilibrium and nonequilibrium conditions in a binary liquid mixture. The free energy of solvation as well as two sets of constitutive relations, one applicable under equilibrium conditions and the other applicable under out-of-equilibrium conditions, are derived. In Section III, we apply the general DSCFT to solvent reorganization energy in ET reactions. For comparison, we also briefly describe a uniform dielectric treatment for calculating the solvent composition dependence of the reorganization energy, based on the dielectric permittivities of the homogeneous solvent mixtures. In Section IV, we study the relationship between the solvent composition and the reorganization energy for electron exchange reactions between Fe^{2+} and Fe^{3+}, where both the donor and acceptor are charged, and between Ag^0 and Ag^{1+}, where the ET occurs between a neutral and a charged species, in three general categories of binary solvent mixtures. We highlight the connection between the reorganization energy and the local solvent composition profile around the reacting species. Finally, in Section V, we recapitulate the main points in this work and offer some concluding remarks and outlook.

II. DIPOLAR SELF-CONSISTENT-FIELD THEORY (DSCFT) FOR CHARGE SOLVATION IN SOLVENT MIXTURES

In this section, we formulate the dipolar self-consistent-field theory (DSCFT) for charge solvation in liquid mixtures under equilibrium and nonequilibrium conditions. Here, equilibrium refers to a condition in which both the nuclear and the electronic degrees of freedom of the solvent are in equilibrium with the charge on the solute; nonequilibrium refers to a condition where the nuclear degrees of freedom of the solvent are out-of-equilibrium due to their longer relaxation times while the electronic degrees of freedom are allowed to equilibrate.

For simplicity, we consider a charged solute in a binary mixture consisting of solvent A and solvent B, with a bulk composition specified by the mole fraction of one of the species (A for concreteness), x_A; the theory can be easily generalized to multi-component mixtures. We characterize each solvent molecule by its permanent dipole moment $\bar{\mu}_S$, polarizability α_S, and molecular volume v_S ($S = A, B$). The solute is described by its charge distribution $\hat{\rho}_c(\mathbf{r})$ inside a cavity $\mathcal{C}$ that is inaccessible to the solvent molecules. The charge distribution of the system can be described as

$$\hat{\rho}(\mathbf{r}) = \hat{\rho}_c(\mathbf{r}) + \hat{\rho}_{\rm or}(\mathbf{r}) + \hat{\rho}_{\rm el}(\mathbf{r}) \tag{1}$$

where $\hat{\rho}_{\rm or}$ and $\hat{\rho}_{\rm or}$ are the charge densities due to the permanent and the induced dipole moments, respectively, given by

$$\hat{\rho}_{\rm or}(\mathbf{r}) = -\sum_{S,i} \boldsymbol{\mu}_{S,i} \cdot \nabla\delta(\mathbf{r} - \mathbf{r}_{S,i}) \tag{2}$$

$$\hat{\rho}_{\rm el}(\mathbf{r}) = -\sum_{S,i} \mathbf{p}_{S,i} \cdot \nabla\delta(\mathbf{r} - \mathbf{r}_{S,i}) \tag{3}$$

In the above expressions, $\mathbf{r}_{S,i}$, $\boldsymbol{\mu}_{S,i}$, and $\mathbf{p}_{S,i}$ respectively denote the position, the permanent dipole moment, and the induced dipole of the ith molecule of type S, and the summation runs over all solvent molecules. The permanent dipole moments have fixed magnitude $|\boldsymbol{\mu}_{S,i}| = \bar{\mu}_S$.

The energy of the system consists of the Coulomb interaction and the deformation cost of the induced dipoles, and it can be written as

$$U = \frac{1}{2}\int d\mathbf{r} \int d\mathbf{r}' \frac{\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} + \sum_{S,i} \frac{\mathbf{p}_{S,i}^2}{2\alpha_S} \tag{4}$$

where ϵ_0 is the permittivity of the vacuum.

To proceed, we consider a large enough volume V around the charged solute at temperature T that is open

to both solvent species, each with chemical potential μ_S. The particle-based grand partition function is given by

$$\Xi = \sum_{N_A=0}^{\infty}\sum_{N_B=0}^{\infty}\frac{1}{N_A!}\frac{1}{N_B!}e^{\beta\mu_A N_A}e^{\beta\mu_B N_B} \times \prod_{S=A,B}\left(\prod_{i=1}^{N_S}\frac{1}{\eta_S}\int d\mathbf{r}_{S,i}\int d\boldsymbol{\mu}_{S,i}\int d\mathbf{p}_{S,i}\right) \times\delta\left[\sum_S v_S\hat{n}_S(\mathbf{r})-1\right]e^{-\beta U} \quad (5)$$

where N_S is the number of molecules of solvent S, $\beta = 1/k_BT$, and η_S is the analog of thermal de Broglie wavelength that makes the configurational integral dimensionless. The value of η_S is inconsequential as it only contributes to a reference energy. The integral runs over the configurational space of the solvent molecules, with integration over $\mathbf{r}_{S,i}$ extends the space outside the solute cavity, and integration over $\boldsymbol{\mu}_{S,i}$ spans the 4π solid angle (as the magnitude of the permanent dipole is fixed). $\hat{n}_S(\mathbf{r}) = \sum_{i=1}^{N_S}\delta(\mathbf{r}-\mathbf{r}_{S,i})$ is the number density operator for solvent S. v_S is the molecular volume of solvent S which reflects the effects of the non-electrostatic intermolecular forces in giving rise to the particular density of the liquid at a given temperature and pressure. The δ-functional in Eq. (5) enforces an incompressibility condition for the liquid mixture, and amounts to assuming no volume change upon mixing.

Using statistical field techniques, we decouple the quadratic interactions between the charge density with a series of identity transformations. The procedure for the transformations is similar to that presented in our early work in Ref. 54, and it leads to the following exact field-theoretic partition function:

$$\Xi = \int\mathcal{D}\rho_{\mathrm{or}}\int\mathcal{D}w_{\mathrm{or}}\int\mathcal{D}\rho_{\mathrm{el}}\int\mathcal{D}w_{\mathrm{el}}\int\mathcal{D}w \times\left(\prod_S\int\mathcal{D}\varphi_S\int\mathcal{D}w_S\right)e^{-\beta H} \quad (6)$$

with the effective field Hamiltonian H given by

$$\begin{aligned}&\beta H[\rho_{\mathrm{or}}, w_{\mathrm{or}}, \rho_{\mathrm{el}}, w_{\mathrm{el}}, w, \varphi_S, w_S]\\ &= \int d\mathbf{r}\int d\mathbf{r}'\,\frac{\beta\rho(\mathbf{r})\rho(\mathbf{r}')}{8\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} + i\sum_S\int d\mathbf{r}\, w_S(\mathbf{r})\varphi_S(\mathbf{r})\\ &-i\int d\mathbf{r}\, w_{\mathrm{or}}(\mathbf{r})\rho_{\mathrm{or}}(\mathbf{r}) - i\int d\mathbf{r}\, w_{\mathrm{el}}(\mathbf{r})\rho_{\mathrm{el}}(\mathbf{r})\\ &-i\int d\mathbf{r}\, w(\mathbf{r})\left(\sum_S\varphi_S(\mathbf{r})-1\right) - \sum_S e^{\beta\mu_S}Q_S\end{aligned} \quad (7)$$

where $\rho(\mathbf{r}) = \hat{\rho}_c(\mathbf{r}) + \rho_{\mathrm{or}}(\mathbf{r}) + \rho_{\mathrm{el}}(\mathbf{r})$, and Q_S is the single-particle partition function in the fields $w_S(\mathbf{r})$, $w_{\mathrm{or}}(\mathbf{r})$ and $w_{\mathrm{el}}(\mathbf{r})$,

$$Q_S = \frac{4\pi\bar{\mu}_S^2}{\eta_S}\left(\frac{2\pi\alpha_S}{\beta}\right)^{\frac{3}{2}}\int d\mathbf{r}\,\left\{\Gamma(\mathbf{r})\frac{\sin(\bar{\mu}_S|\nabla w_{\mathrm{or}}(\mathbf{r})|)}{\bar{\mu}_S|\nabla w_{\mathrm{or}}(\mathbf{r})|} \times\exp\left[iv_S w_S(\mathbf{r}) - \frac{\alpha_S}{2\beta}(\nabla w_{\mathrm{el}}(\mathbf{r}))^2\right]\right\} \quad (8)$$

Here, $\Gamma(\mathbf{r})$ serves to limit the integration to space outside the solute cavity, with $\Gamma(\mathbf{r}) = 0$ if $\mathbf{r}\in\mathcal{C}$ and 1 otherwise. The transformation to the field-theoretic partition function has introduced the coarse-grained charge density fields ρ_{or} and ρ_{el} for the solvent permanent and induced dipoles, respectively; w_{or} and w_{el} are the scaled orientational and electronic electric potentials that are the conjugate fluctuating fields to ρ_{or} and ρ_{el}, respectively. w is a coarse-grained pressure-like field arising from the incompressibility condition. φ_S is the coarse-grained spatially-dependent volume fraction of species S, with w_S being the volume fraction potential that is conjugate to φ_S.

The functional integration in the field-based partition function in Eq. (6) cannot be evaluated exactly in closed form. To proceed, we take the saddle-point approximation by extremizing the effective Hamiltonian H with respect to its functional arguments. In the equilibrium condition, we obtain the constitutive relations by extremizing H with respect to all of its functional arguments. In the nonequilibrium condition, the solvent composition in the system and the orientational polarization are out of equilibrium because of the longer response time of nuclear degrees of freedom; therefore, the functions ρ_{or} and φ_S keep their values from the previous equilibrium state, and we perform a constrained extremization of H with respect to the rest of the functional arguments. Details of the derivation are provided in the supporting information. In order to work with real quantities and for the convenience of relating our theory to classical electrostatics, we make a change of variables $w_{\mathrm{or}} = -i\beta\phi_{\mathrm{or}}$, $w_{\mathrm{el}} = -i\beta\phi_{\mathrm{el}}$, and $w_S = i\beta u_S$. The resulting set of constitutive relations for charge solvation under equilibrium condition is

$$\nabla\cdot\mathbf{D} = \hat{\rho}_c(\mathbf{r}) \quad (9)$$

$$\varphi_S(\mathbf{r}) = \Gamma(\mathbf{r})\varphi_S^{(\infty)}\exp\left[-\beta u(\mathbf{r})v_S + \frac{\beta\alpha_S}{2}|\nabla\phi(\mathbf{r})|^2\right] \times\frac{\sinh(\beta\bar{\mu}_S|\nabla\phi(\mathbf{r})|)}{\beta\bar{\mu}_S|\nabla\phi(\mathbf{r})|} \quad (10)$$

$$\sum_S\varphi_S(\mathbf{r}) = 1 \quad (11)$$

where $\mathbf{D}$ is the electric displacement given by

$$\mathbf{D} = -\epsilon_0[1+\chi_{\mathrm{el}}(\mathbf{r})+\chi_{\mathrm{or}}(\mathbf{r})]\nabla\phi(\mathbf{r}) \quad (12)$$

and $\chi_{\mathrm{or}}(\mathbf{r})$ and $\chi_{\mathrm{el}}(\mathbf{r})$ are the electric susceptibilities due to the permanent and the induced dipoles, respectively,

given by

$$\chi_{\rm or}(\mathbf{r}) = \Gamma(\mathbf{r}) \sum_S \frac{\beta\bar{\mu}_S^2 \varphi_S(\mathbf{r})}{\epsilon_0 v_s} \frac{\mathcal{L}(\beta\bar{\mu}_S|\nabla\phi(\mathbf{r})|)}{\beta\bar{\mu}_S|\nabla\phi(\mathbf{r})|} \tag{13}$$

$$\chi_{\rm el}(\mathbf{r}) = \Gamma(\mathbf{r}) \sum_S \frac{\varphi_S(\mathbf{r})\alpha_S}{v_S\epsilon_0} \tag{14}$$

with $\mathcal{L}(x) = (\coth x - 1/x)$ being the Langevin function. We recognize that Eq. (9) is just the Poisson equation. Eqs. (9) – (11) are to be solved for the fields ϕ, φ_S and u. The bulk volume fraction $\varphi_S^{(\infty)}$ of solvent S is related to the mole fractions of the species through $\varphi_S^{(\infty)} = x_S v_S / \left(\sum_{S'} x_{S'} v_{S'}\right)$. The subscripts on the functions ϕ and u are omitted because at full equilibrium the extremization procedure results in $\phi = \phi_{\rm or} = \phi_{\rm el}$ and $u = u_A = u_B$.

Under the nonequilibrium condition in which the nuclear degrees of freedom (reflected in the values of φ_S and $\phi_{\rm or}$) are fixed from the corresponding equilibrium state, the constitutive relations are

$$\nabla \cdot \mathbf{D} = \hat{\rho}_c(\mathbf{r}) \tag{15}$$

$$\varphi_S(\mathbf{r}) = \Gamma(\mathbf{r})\varphi_S^{(\infty)} \exp\left[-\beta u_S(\mathbf{r}) v_S + \frac{\beta\alpha_S}{2}|\nabla\phi_{\rm el}(\mathbf{r})|^2\right] \times \frac{\sinh(\beta\bar{\mu}_S|\nabla\phi_{\rm or}(\mathbf{r})|)}{\beta\bar{\mu}_S|\nabla\phi_{\rm or}(\mathbf{r})|} \tag{16}$$

where the electric displacement $\mathbf{D}$ is now given by

$$\mathbf{D} = -\epsilon_0 \left[(1 + \chi_{\rm el}(\mathbf{r}))\nabla\phi_{\rm el}(\mathbf{r}) + \chi_{\rm or}(\mathbf{r})\nabla\phi_{\rm or}(\mathbf{r})\right] \tag{17}$$

Note that Eqs. (15) and (16) have similar form to Eqs. (9) and (10), except that we have to distinguish between the electric potentials $\phi_{\rm el}$ and $\phi_{\rm or}$, and between the conjugate fields to the composition u_A and u_B. The value for $\chi_{\rm el}$ is given by Eq. (14). Eqs. (15) and (16) are then solved for the values of $\phi_{\rm el}$ and u_S, with $\chi_{\rm or}$, $\phi_{\rm or}$, φ_S, and Γ from the corresponding equilibrium state that has the same nuclear configuration.[55] We note that Γ describes the space accessible to solvent molecules, and therefore, it is related to the nuclear configuration of the solvent. Since φ_S remains unchanged from the corresponding equilibrium value, Eq. (11) is automatically satisfied, and the electric susceptibilities $\chi_{\rm el}$ and $\chi_{\rm or}$ in the nonequilibrium state turn out to be equal to those in the corresponding equilibrium state.

The free energy of solvation is obtained by evaluating the field-theoretic Hamiltonian H at the saddle-point values of its functional arguments. Upon simplification, the free energy of solvation G can be written as

$$G[\mathbb{C}, \hat{\rho}_c] = \int d\mathbf{r} \left[-\sum_S \left(u_S(\mathbf{r})\varphi_S(\mathbf{r}) + \frac{\varphi_S(\mathbf{r})}{\beta v_S}\right) + \epsilon_0 \left(\frac{1}{2} + \chi_{\rm el}(\mathbf{r})\right)|\nabla\phi_{\rm el}(\mathbf{r})|^2 + \epsilon_0\chi_{\rm or}|\nabla\phi_{\rm or}(\mathbf{r})|^2\right] \tag{18}$$

where $\mathbb{C} = \{\varphi_S, \phi_{\rm or}, \chi_{\rm or}, \mathcal{C}\}$ is the nuclear configuration set, which contains all necessary information describing the solvent nuclear configuration. In the above free energy expression, the values of $\chi_{\rm el}$, $\phi_{\rm el}$, and u_S used for evaluating G are to be calculated using the set of constitutive relations appropriate for the solvation condition (i.e., equilibrium vs. nonequilibrium).

The constitutive relations under equilibrium condition (Eqs. (9) – (11)) and nonequilibrium condition (Eqs (15) and (16)), and the free energy of solvation (Eq. (18)) are the key equations in the theory, and can be applied to study the energetics of general ET processes in solvent mixtures. In the following section, we focus on electron transfer between simple ions, and outline the calculation of the solvent reorganization energy.

III. CALCULATION OF SOLVENT REORGANIZATION ENERGY

Broadly speaking, the solvent composition impacts the ET kinetics through two main effects: first, the composition-dependent dielectric properties of the solvent affects the donor-acceptor association constant; second, the local composition of the solvents around the reacting species strongly influences the solvent reorganization energy. Both effects are important for the rate of ET reactions. However, in this article, we focus on how the local solvent composition around the donor-acceptor complex affects the solvent reorganization energy.

A. The DSCFT Calculation

We consider electron transfer between two simple ions in the form $D^m + A^n \to D^{m+1} + A^{n-1}$, where D and A respectively denote the electron donor and the acceptor, with their centers located at $\mathbf{R}_D$ and $\mathbf{R}_A$, respectively. The solute charge distribution is described by $\hat{\rho}_c^{(\mathcal{R})}(\mathbf{r}) = me\delta(\mathbf{r} - \mathbf{R}_D) + ne\delta(\mathbf{r} - \mathbf{R}_A)$ in the reactant state, and $\hat{\rho}_c^{(\mathcal{P})}(\mathbf{r}) = (m+1)e\delta(\mathbf{r} - \mathbf{R}_D) + (n-1)e\delta(\mathbf{r} - \mathbf{R}_A)$ in the product state, where e is the elementary charge. The solute cavity $\mathcal{C}^{(\mathcal{R})}$ in the reactant state has the shape of two spheres, described by $\{\mathbf{r} : |\mathbf{r} - \mathbf{R}_D| < a_D^{(\mathcal{R})}$ or $|\mathbf{r} - \mathbf{R}_A| < a_A^{(\mathcal{R})}\}$, where $a_D^{(\mathcal{R})}$ and $a_A^{(\mathcal{R})}$ are the ionic radii (or atomic radii if the species is neutral) of D^m and A^n. The solute cavity $\mathcal{C}^{(\mathcal{P})}$ in the product state is defined similarly, with $a_D^{(\mathcal{P})}$ and $a_A^{(\mathcal{P})}$ being the ionic radii of D^{m+1} and A^{n-1}.[56]

The solvent reorganization energy λ is the free energy difference between the following two states: (i) the equilibrium state under the product charge distribution and (ii) the nonequilibrium state under the product charge distribution but with the nuclear configuration from the reactant state. The nuclear configuration of a state includes the solvent composition, orientational polarization, and the accessible space to the solvent outside the

solute cavity, and we denote this information in a nuclear configuration set $\mathbb{C}^{(\mathcal{S})} = \{\varphi_S^{(\mathcal{S})}, \phi_{\rm or}^{(\mathcal{S})}, \chi_{\rm or}^{(\mathcal{S})}, \mathcal{C}^{(\mathcal{S})}\}, (\mathcal{S} = \mathcal{R}, \mathcal{P})$. Algebraically, we express λ as

$$\lambda = G[\mathbb{C}^{(\mathcal{R})}, \hat{\rho}_c^{(\mathcal{P})}] - G[\mathbb{C}^{(\mathcal{P})}, \hat{\rho}_c^{(\mathcal{P})}] \tag{19}$$

In computing the reorganization energy, the integral only needs to be evaluated for the region outside the cavity by referencing the free energy to a vacuum state with the same charge distribution. Details for the procedure are given in Appendix B of Ref. 54.

To simplify the calculation, we solve Eqs. (9) and (15) by assuming that the electric displacement $\mathbf{D}$ can be written as a superposition of the displacement due to each individual point charge as

$$\mathbf{D}(\mathbf{r}) = \frac{q_D}{4\pi r_D^2}\hat{\mathbf{r}}_D + \frac{q_A}{4\pi r_A^2}\hat{\mathbf{r}}_A \tag{20}$$

where $\mathbf{r}_{D/A} = \mathbf{r} - \mathbf{R}_{D/A}$ and $\hat{\mathbf{r}}_{D/A}$ indicates the unit vector in the direction of $\mathbf{r}_{D/A}$.

We perform numerical evaluations on a two-center bispherical coordinate (σ, τ, φ), which relates to the cylindrical coordinate (r, z, φ) by $z = a_0 \sinh\sigma/(\cosh\sigma - \cos\tau)$ and $r = a_0 \sin\sigma/(\cosh\sigma - \cos\tau)$. Each constant-$\sigma$ surface in the bispherical coordinate is a circle of radius $a_0/|\sinh\sigma|$ with its center located at $z = a_0 \coth\sigma$. The value of a_0 is determined by the ionic radii of the donor and the acceptor and their distance, and by requiring that the cavity boundaries of the donor and the acceptor are each a surface of constant σ, and that the region accessible by the solvent is simply described by $\sigma_A < \sigma < \sigma_D$. This is achieved by simultaneously solving

$$\frac{a_0}{|\sinh\sigma_D|} = a_D \tag{21a}$$

$$\frac{a_0}{|\sinh\sigma_A|} = a_A \tag{21b}$$

$$a_0 \coth\sigma_D - a_0 \coth\sigma_A = d \tag{21c}$$

Geometrically, these set of equations describe the donor cavity surface by $\sigma = \sigma_D = \cosh^{-1}\left(\frac{a_D^2 - a_A^2 + d^2}{2a_D d}\right)$, and the acceptor cavity surface by $\sigma = \sigma_A = -\cosh^{-1}\left(\frac{a_A^2 - a_D^2 + d^2}{2a_A d}\right)$, and $a_0 = a_D \sinh\sigma_D$. Due to the cylindrical symmetry in the problem, we only have to perform calculations on the two-dimensional $\sigma\tau$-plane. The integration for the free energy is carried out on a 60×170 $\sigma\tau$-grid between $\sigma \in (\sigma_A, \sigma_D)$ and $\tau \in (0, \pi)$. The electric potential field ϕ in the equilibrium state is found by iteration until the next iteration produces a reduced potential field $\nabla\phi/[\frac{e}{4\pi\epsilon_0(2a_D a_A/(a_D+a_A))}]$ within 10^{-8} from its current value at all grid points.

B. The Uniform Dielectric Treatment

As mentioned in the introduction, a key effect that influences the ET reorganization energy in a mixture is preferential solvation due to the difference in the local solvent composition around the charged redox species from the bulk. In order to highlight the effects of preferential solvation in a liquid mixture, in this subsection we examine the consequence of ignoring the preferential solvation on the reorganization energy by assuming the solvent to be a uniform dielectric medium. In Section IV, we will compare results from our DSCFT calculation with results from the uniform dielectric treatment presented in this subsection. We start with the familiar Marcus equation[2] for reorganization energy

$$\lambda_{\rm cl} = (\Delta e)^2 \left(\frac{1}{2a_D} + \frac{1}{2a_A} - \frac{1}{d}\right)\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_s}\right) \tag{22}$$

where ε_∞ and ε_s are respectively the optical and static dielectric permittivities of the solvent. If we assume the solvent mixture to be spatially uniform, then the dielectric response can be characterized by the optical and static dielectric permittivities of a homogeneous bulk mixture, which are commonly approximated using the Clausius-Mossotti equation[57,58] and the Onsager equation[59,60], respectively given by

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \sum_{S=A,B} \varphi_S^{(\infty)} \frac{\epsilon_{\infty,S} - 1}{\epsilon_{\infty,S} + 2} \tag{23}$$

and

$$\frac{(\epsilon_s - 1)(2\epsilon_s + 1)}{\epsilon_s} = \sum_{S=A,B} \varphi_S^{(\infty)} \frac{(\epsilon_{s,S} - 1)(2\epsilon_{s,S} + 1)}{\epsilon_{s,S}} \tag{24}$$

where $\epsilon_{\infty,S}$ and $\epsilon_{s,S}$ are respectively the corresponding optical and static dielectric permittivities of pure solvent S.

The Pekar factor $P = 1/\epsilon_\infty - 1/\epsilon_s$ is the only solvent-dependent factor in the expression for reorganization energy in Eq. (22). Given the reorganization energies λ_A and λ_B in pure solvents A and B, respectively, the reorganization energy in an A/B mixture follows from Eq. (22) to be

$$\lambda_{\rm cl} = \lambda_A + \frac{P - P_A}{P_B - P_A}(\lambda_B - \lambda_A) \tag{25}$$

where P_S is the Pekar factor for the pure solvent S. Here, for consistency and to provide a meaningful interpolation that matches the pure solvent results, we use the DSCFT-predicted reorganization energies for the pure solvents.[61] Note that Eq. (25) is invariant with respect to switching labels A and B. We refer to Eq. (25) as the uniform dielectric treatment for calculating the mixture reorganization energy.

IV. SOLVENT REORGANIZATION ENERGY OF SELF-EXCHANGE REACTIONS IN BINARY MIXTURES

In this section, we study the solvent reorganization energy for electron transfer in binary liquid mixtures.

TABLE I. Parameters for the pure solvents involved in the binary mixed solvents considered in this paper. The permanent dipole $\bar{\mu}$, the molecular polarizability α, and the molecular volume v are used in the DSCFT calculation. v is the volume per molecule calculated from the liquid density at 25°C. The static and optical dielectric permittivities, ϵ_s and ϵ_∞ are listed here for reference and for calculations using the uniform dielectric treatment.

	DSCFT			Bulk	
Solvent	$\bar{\mu}$ [D]	α [Å^3]	v [Å^3]	ϵ_s	ϵ_∞
Water	1.85	1.45	30.0	80.1	1.78
Methanol	1.70	3.29	67.2	33.0	1.77
DMSO	3.96	8.00	117.8	47.2	2.19
2-Propanol	1.58	6.97	127.8	20.2	1.90
Pyridine	2.22	9.65	133.8	13.3	2.28

We consider two simple electron-exchange reactions: (i) $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ and (ii) $Ag^0 + Ag^{1+} \rightarrow Ag^{1+} + Ag^0$. In case (i), the electron transfer occurs between two multiply-charged species, whereas in case (ii) the electron transfer occurs between a singly-charged species and a neutral species. We note that, even though we apply the DSCFT to self-exchange reactions in the present paper, the calculation of reorganization energy with the DSCFT is applicable to general reactions. The radii of the electron-transferring species are taken to be their crystallographic ionic or atomic radii, whose values are 0.92 Å, 0.785 Å, 1.29 Å, and 1.60 Å for Fe^{2+}, Fe^{3+}, Ag^{1+}, and Ag^0, respectively. The distance between the centers of the donor and the acceptor is kept at $d = 5.5$ Å.

Because charge solvation has different time and length scale dependence on the permanent and induced dipoles, we classify binary solvent mixtures into the following three general categories based on the relative static and optical dielectric permittivities of the two liquid components, and examine a representative solvent mixture from each category:

1. The two components have comparable optical dielectric permittivities, but one component has a higher static dielectric permittivity than the other; e.g. *water/methanol mixture*

2. The two components have comparable static dielectric permittivities, but one component has a higher optical dielectric permittivity than the other; e.g. *2-propanol/pyridine mixture*

3. One of the components has a higher static dielectric permittivity but a lower optical dielectric permittivity than the other component; e.g. *water/DMSO mixture*

We note that, in comparing the dielectric permittivities of polar liquids, a difference of 10 in static dielectric permittivity is considered quite moderate, while a difference of 0.1 in optical dielectric permittivity can be considered quite large. In referring to the binary solvent mixtures, we adopt the notation that the component with a higher static dielectric is followed by the component with the lower static dielectric permittivity, separation by a slash. For example, an A/B mixture is one where A has a higher static dielectric permittivity than B. Henceforth, we use the mole fraction to denote the mixture composition. We calculate the solvent composition and the reorganization energy in the chosen example of solvent mixture mentioned in each category. In Table I, we list the permanent dipole $\bar{\mu}$, the molecular polarizability α, and the molecular volume v for the five solvent species studied in this work, together with their experimental static dielectric permittivities ϵ_s and optical dielectric permittivities ϵ_∞.

A. Electron self-exchange between charged species

We first examine the self-exchange reaction $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ in binary mixtures. Since both the donor and the acceptor are multiply charged, preferential solvation takes place around both the donor and the acceptor. The local solvent composition in the immediate vicinity of the donor and acceptor is insensitive to the global solvent composition. We thus expect that the electron transfer reorganization energy – which is largely determined by the local composition of the solvent around the donor-acceptor complex – to be a weak function of the bulk solvent composition in a broad composition range.

The first case we consider is the water/methanol mixture. Since the two solvent components have similar optical dielectric permittivities, water is expected to be enriched around both the donor and the acceptor because of its higher static dielectric permittivity. In Fig. 1(a), we plot the equilibrium solvent composition around the donor-acceptor complex for a 50:50 water/methanol mixture in cylindrical coordinate, in which the centers of Fe^{2+} and Fe^{3+} are located on the z-axis. The solute cavity is represented by the white semispherical region, labeled with the charge of the ion. The region around the electron-transferring species appears bright-yellow, indicating that the ET species is essentially surrounded by pure water. As a result, the solvent reorganization energy in a water/methanol mixture over most of the composition range approximately equals to that in pure water, except at exceedingly low water concentration. This is shown in the plot of solvent reorganization energy vs. mole fraction of water in Fig. 2(a). In the Supplementary Information, we also provide a comparison between the activation energies calculated by the DSCFT and by the MD simulation based on nonpolarizable solvent models; the qualitative trend in the simulation is well captured by the DSCFT.

The observation here provides a qualitative explanation to the experimental result by Wada and Endo.[35] These authors found that the rate of Fe^{2+}/Fe^{3+} exchange in the water/methanol mixture stays constant for mole fraction of methanol between 0 and 0.3. At higher concentrations of methanol, however, the experiment observed a gradual decrease in the rate of reaction with

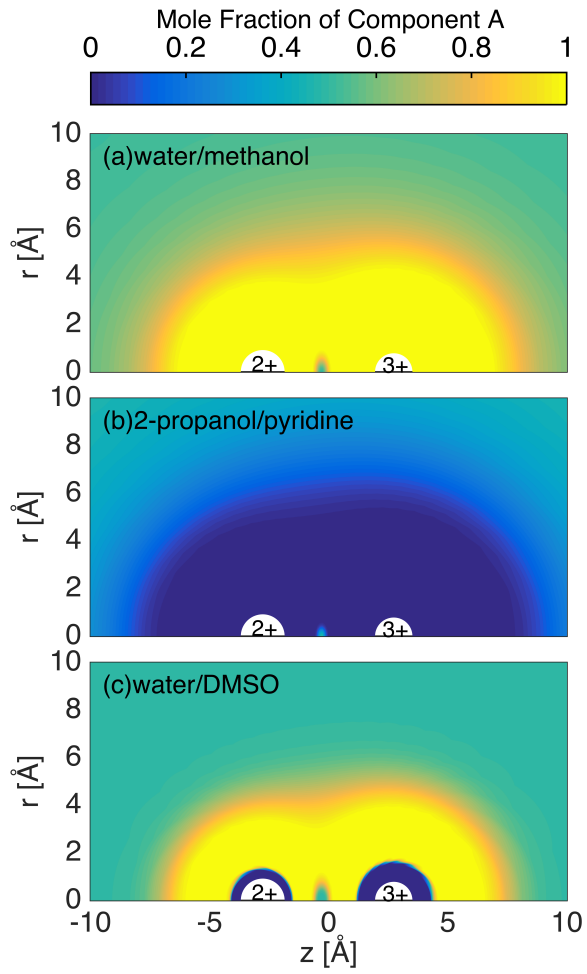

FIG. 1. Equilibrium composition (mole fraction of solvent component A) around the donor-acceptor complex at the reactant state for the $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ reaction in a 50:50 mixture of (a) water and methanol, (b) 2-propanol and pyridine, and (c) water and DMSO. The mole fraction of A is plotted on a cylindrical r-z coordinate with the centers of the donor and the acceptor located on the $r = 0$ axis. The center of the donor (Fe^{2+}) and the acceptor (Fe^{3+}) are located at $z = -2.75$ Å and $z = 2.75$ Å respectively. The white semi-spherical regions indicate the space occupied by the donor and the acceptor, which is inaccessible to the solvent molecules.

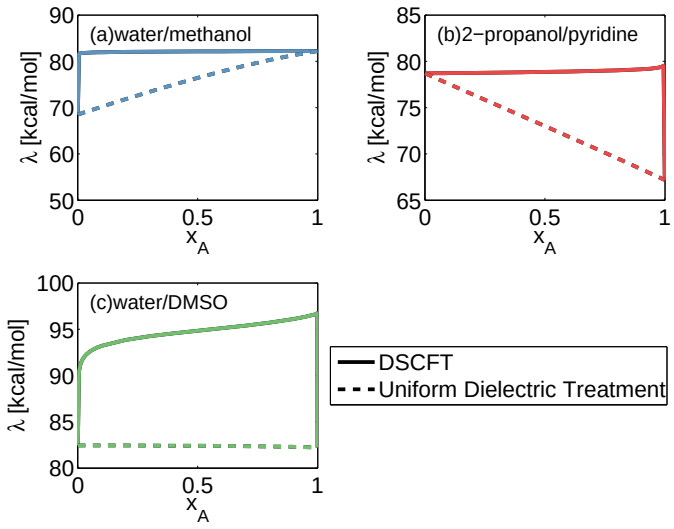

FIG. 2. Solvent reorganization energy (λ) vs. the mole fraction of component A (x_A) for electron self-exchange reaction $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$ in (a) water/methanol, (b)2-propanol/pyridine, and (c) water/DMSO mixtures. The solid squares are results calculated with the DSCFT, while the dashed lines are results calculated from the uniform dielectric treatment using Eq. (25).

increasing methanol content. A likely explanation is the increased energy penalty for Fe^{2+} and Fe^{3+} to approach to a reactive distance (of approximately 6 Å) from each other, as a result of the decreased solvent dielectric permittivity with increasing methanol content.

The second case is the 2-propanol/pyridine mixture. While 2-propanol and pyridine have comparable static dielectric permittivities, pyridine has a significantly higher optical dielectric permittivity, and therefore is more polarizable. Under the strong electric fields around a multiply-charged ion, the more polarizable pyridine molecule develops a significantly larger induced dipole. As a result, pyridine interacts more favorably with the ions and is enriched around the ions. In Fig. 1(b), we present the equilibrium solvent composition in a 50:50 2-propanol/pyridine mixture. The blue region suggests that pyridine is enriched around the donor-acceptor complex, despite having a smaller static dielectric permittivity than 2-propanol. As the immediate vicinity of Fe^{2+} and Fe^{3+} are exclusively occupied by pyridine, the solvent reorganization energy for Fe^{2+}/Fe^{3+} exchange in 2-propanol/pyridine mixtures should be nearly equal to that in pure pyridine, except at very low pyridine concentration. This behavior is confirmed by the plot of solvent reorganization energy vs. mole fraction of 2-propanol shown in Fig. 2(b).

The third case is Fe^{2+}/Fe^{3+} self-exchange process in the water/DMSO mixture. In this case, water has a higher static dielectric permittivity, but DMSO has a higher optical dielectric permittivity. Because both larger permanent dipole moment and larger polarizability lead to favorable interactions with the ions, we expect both water and DMSO to be present in the immediate vicinity of both Fe^{2+} and Fe^{3+}. Fig. 1(c) shows the equilibrium solvent composition around the $Fe^{2+} - Fe^{3+}$ complex in a 50:50 water/DMSO mixture. The composition profile clearly indicates the presence of both water and DMSO in the neighborhood of the donor and the acceptor – while water is the preferred solvent in most regions within about 5 Å from the centers of the ions, DMSO is enriched in the immediate vicinity of the ions, where the electric field is the strongest. We should caution that such coarse-grained composition profile must be inter-

preted with discretion, as the size of individual solvent molecules could be bigger than the structural features in the composition profile. Nevertheless, if we average the composition over the typical size of a molecule, the composition profile in Fig. 1(c) suggests that there are more DMSO molecules around the Fe^{3+} than the Fe^{2+} because of the stronger electric field around the charge +3 ion. The unequal solvent concentration around the donor and the acceptor gives rise to a compositional contribution to the solvent reorganization energy, in addition to the contribution from the orientational polarization. Consequently, the solvent reorganization energy for Fe^{2+}/Fe^{3+} exchange in water/DMSO is significantly higher than that in either of the pure components, as shown in Fig. 2(c). These results provide a qualitative understanding for the earlier experimental observation by Wada and Aoki, who found the rate of reaction for the Fe^{2+}/Fe^{3+} exchange vary nonmonotonically with the solvent composition in a water/DMSO mixture, with a minima in the reaction rate at some intermediate concentration of DMSO.[34]

To highlight the effect of preferential solvation, in Fig. 2 we include results for the reorganization energy calculated using the uniform dielectric treatment, Eq. (25) (shown as dashed lines in the figure). In all cases, the reorganization energy calculated by the DSCFT is larger than that predicted by the uniform dielectric treatment. This suggests that the solvent reorganization energy for the Fe^{2+}/Fe^{3+} exchange reaction is primarily determined by the local solvent composition around the donor-acceptor complex, and is insensitive to the global solvent composition.

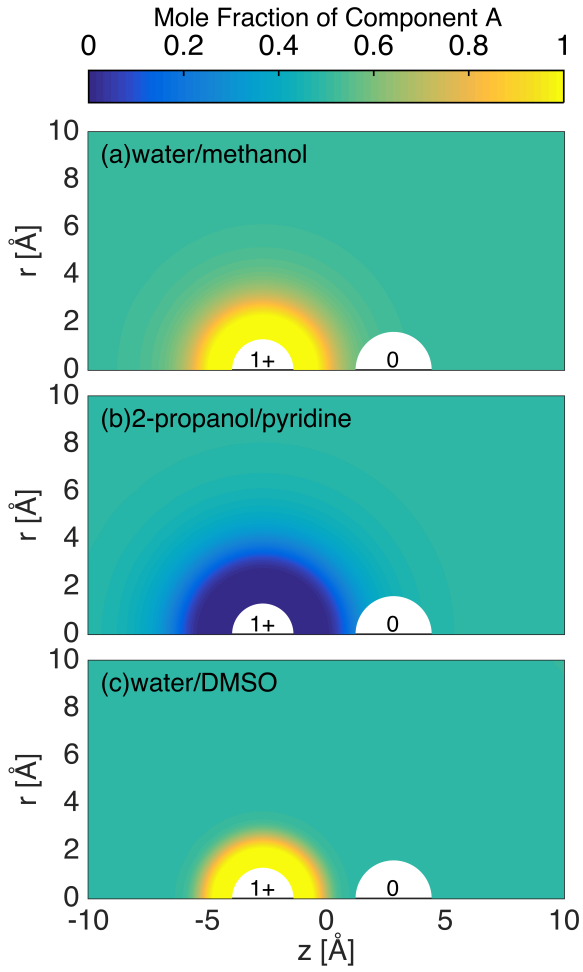

FIG. 3. Equilibrium composition (mole fraction of solvent component A) around the donor-acceptor complex at the reactant state for the $Ag^{1+} + Ag^0 \rightarrow Ag^0 + Ag^{1+}$ reaction in a 50:50 mixture of (a) water and methanol, (b) 2-propanol and pyridine, and (c) water and DMSO. The mole fraction of A is plotted on a cylindrical r-z coordinate with the centers of the donor and the acceptor located on the $r = 0$ axis. The center of the donor (Ag^{1+}) and the acceptor (Ag^0) are located at $z = -2.75$ Å and $z = 2.75$ Å respectively. The white semispherical regions indicate the space occupied by the donor and the acceptor, which is inaccessible to the solvent molecules.

B. Electron self-exchange between a charged and a neutral species

In contrast to Fe^{2+}/Fe^{3+} exchange reaction studied in the last subsection where both the donor and acceptors carry multiple charges, in this subsection we explore the reaction $Ag^{1+}+Ag^0 \rightarrow Ag^0+Ag^{1+}$, an exchange between a singly-charged and a neutral species, again in the three classes of binary solvent mixtures. In this reaction, the vicinity of the charged Ag^{1+} is enriched in the preferred solvent component, while the surrounding of the neutral Ag^0 is mostly at the bulk solvent composition. Unlike the previous case of charge transfer between multiply-charged solutes, where the solvent reorganization energy primarily depends on the local solvent composition, this reaction, involving a neutral species, is expected to exhibit a stronger dependence of its reorganization energy on the bulk solvent composition.

First, we consider the Ag^{1+}/Ag^0 exchange in the water/methanol mixture. At equilibrium, water is enriched around the Ag^{1+} ion, while the solvent composition around the Ag^0 atom is essentially at the bulk composition, as presented in the equilibrium solvent composition profile for a 50:50 water/methanol mixture in Fig. 3(a). Because of the enrichment of water around Ag^{1+}, addition of a small amount of water to pure methanol should lead to a large increase in the solvent reorganization energy. Further addition of water continues to change the solvent composition around the Ag^0, causing a gradual increase in reorganization energy with increasing water content in the solvent. This dependence of reorganization energy on the solvent composition is observed in Fig. 4(a). Because of the preferential solvation around Ag^{1+}, the reorganization energy at all compositions are above that predicted by the uniform dielectric treatment shown as a dashed curve in Fig. 4(a).

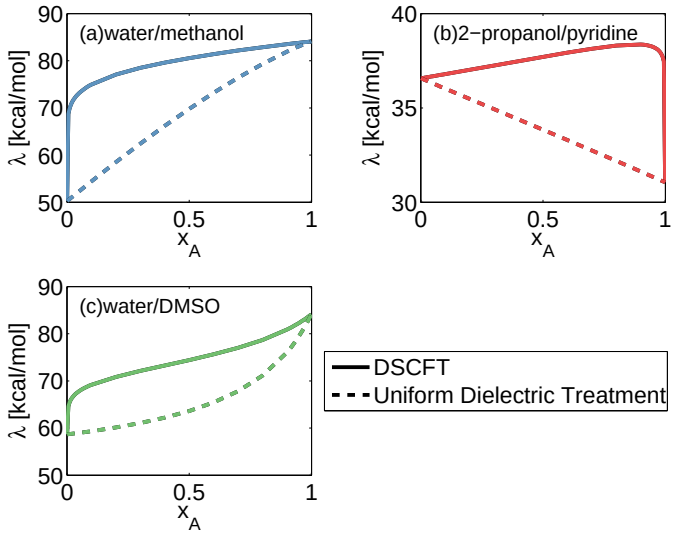

FIG. 4. Solvent reorganization energy (λ) vs. the mole fraction of component A (x_A) for electron self-exchange reaction $Ag^{1+} + Ag^0 \rightarrow Ag^0 + Ag^{1+}$ in (a) water/methanol, (b)2-propanol/pyridine, and (c) water/DMSO mixtures. The solid squares are results calculated with the DSCFT, while the dashed line are results calculated from the uniform dielectric treatment using Eq. (25).

We now consider the 2-propanol/pyridine mixture. In this case, pyridine is enriched around the Ag^{1+} ion because of its higher optical dielectric permittivity, as observed in the equilibrium composition of a 50:50 2-propanol/pyridine mixture in Fig. 3(b). We plot the solvent reorganization energy vs. the bulk mole fraction of 2-propanol in Fig. 4(b). Because of preferential solvation of pyridine around the Ag^{1+} ion, addition of a small amount of pyridine to pure 2-propanol leads to a steep increase in the solvent reorganization energy. Further addition of pyridine gradually change the solvent reorganization energy towards the value in pure pyridine. As in the previous cases, preferential solvation results in a larger solvent reorganization energy than that predicted by the uniform dielectric treatment.

Next we consider the water/DMSO mixture. Since water has a higher static dielectric permittivity and DMSO has a higher optical dielectric permittivity, it is not obvious which component in enriched in the vicinity of Ag^{1+}. Our DSCFT calculation indicates that it is water that is enriched around Ag^{1+}, as shown in Fig. 3(c), because the DMSO molecules are not sufficiently polarized by the low charge on Ag^{1+} to outweigh the Ag^{1+}-water interaction. Therefore, as shown in Fig. 4(c), the addition of a small amount of water to pure DMSO creates a sharp increase in the solvent reorganization energy, while further addition leads to gradual increase in the solvent reorganization energy towards the value in pure water.

V. CONCLUSION

In this work, we have developed a molecularly-based theory for equilibrium and nonequilibrium charge solvation in mixed solvents, and applied the theory to the solvent reorganization energy of ET reactions. Using statistical field methods with the saddle-point approximation, the theory naturally leads to two sets of constitutive relations, one applicable under full equilibrium condition and the other applicable under nonequilibrium condition, as well as a simple, analytical expression for the solvation free energy. The theory considers both the nuclear and the electronic degrees of freedom of the solvent dipoles, and self-consistently accounts for the spatially-varying composition and dielectric response of the mixed solvent around the reacting species. As numerically solving the constitutive relations requires minimal computational effort, the theory provides a convenient and efficient tool for evaluating the ET reorganization energy in mixed solvents.

Our results show that the composition dependence of the solvent reorganization energy is largely determined by the local solvent composition around the reacting species, which is often very different from the bulk solvent composition due to preferential solvation. This observation is in agreement with Ref. 62, which compared the DSCFT-predicted solvation energies to experimental values and found that the equilibrium ion solvation energy in a mixture is predominantly attributed to the solvent composition in vicinity of the ion. Generally, the solvent component with the larger static or optical dielectric permittivity is enriched around the charged solutes, and the solvent reorganization energy is dominated by the contribution from the enriched component. However, if one component has a larger static dielectric permittivity and the other has a larger optical dielectric permittivity, as in the case of water/DMSO mixture, the local solvent composition is sensitive to the the solute charge: the solvent composition around the donor and the acceptor can be quite different. Most interestingly, for the Fe^{2+}/Fe^{3+} exchange in water/DMSO mixture, we predict a reorganization energy that is much larger than that in either of the pure components. Such compositional contribution to the reorganization energy is significant in magnitude and represents a new feature addressed by our work.

By consideration of the local solvent composition profiles around the charged solutes, we identify three classes of binary solvent mixtures, each characterized by the different relative magnitudes of the static and optical dielectric permittivities of the two components. This classification can serve as a convenient guide for the general behavior in the composition dependence of reorganization energy in mixed solvents. In all three classes of solvent mixtures considered, we observe large deviation in solvent reorganization energy from the value predicted by the uniform dielectric treatment, illustrating the important effects of preferential solvation.

The DSCFT in this work provides a general and sys-

tematic approach for calculating solvent effects on the ET reorganization energy. While we have only considered ET processes in binary solvent mixtures in this work, it is straightforward to generalize the theory to multi-component mixed solvents. In addition, the shape and the charge distribution of the donor-acceptor complex can be generalized to describe intermolecular or intramolecular charge transfer of macromolecules. At present, the effects of mixed solvent on ET reaction rate remain largely unexplored; we hope that our theory can facilitate further exploration in the subject by providing a fast and reliable approximation to the solvent reorganization energy. An important direction is to combine the DSCFT with transition state sampling methods, such as the string method,[63,64] to locate the reaction path of ET. It will be useful to understand how coupled changes in local solvent composition and orientational polarization influence the activation as the reaction proceeds from the equilibrium to the transition state. Furthermore, we note that as a simple coarse-grained theory, the DSCFT involves several assumptions and approximations that can be improved with further development. For instance, the local liquid structure around the reacting species can be incorporated using liquid-state density functional theory.[65,66] Due to the small number of solvent molecules in the first solvation shell of the ions, such local structures can lead to more pronounced solvent composition effects than captured in the current theory. It will be interesting to explore these effects in future work.

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SUPPORTING INFORMATION

Details of the derivation of the constitutive relations and a comparison between the activation energies calculated with the DSCFT and with the MD simulation for the ferrous/ferric exchange reaction in water/methanol mixture are provided in the supporting information.

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[56] For calculating the reorganization energy, one only needs the ionic radii in the reactant and the product states. The determination of the variation of ionic radii with the reaction coordinate is intrinsically a quantum mechanical problem, which is beyond the scope of the current work. As far as charge solvation is concerned, Eq. 18 allows us to calculate the nonequilibrium solvation free energy for any ionic radii/solute cavity. More details for the treatment of solute cavity are described in Appendix B of our earlier work in in Ref. 54.
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GRAPHICAL TOC ENTRY